Microphase Separation in Diblock and Triblock Copolymers of Styrene and α-Methylstyrene

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ABSTRACT: Diblock and triblock copolymers of styrene (S) and α-methylstyrene (MS) of the types S-MS, S-MS-S, and MS-S-MS were prepared and characterized. Several copolymers of the type MS-S-MS were partially fractionated to show that a considerable composition distribution was present in block copolymers with $\overline{M}_w/\overline{M}_n \geq 1.5$. Microphase separation was observed in many block copolymer samples using a number of DTA and DSC instruments and volume dilatometry; the appearance of the homopolymer T_g's was taken as an indication of microphase separation. The composition and molecular weight at which microphase separation was observed in diblock and in triblock copolymers was compared with the theoretical predictions of Krause. An interaction parameter, χ_{AB}, between 0.0030 and 0.0036 between the homopolymers was deduced from this comparison, in reasonable agreement with that deduced previously from homopolymer mixing data. A possible change in the theoretical treatment which would lead to better agreement with the homopolymer mixing data is discussed.

In previously published work from this laboratory,[4] it was shown that diblock copolymers of styrene (S) and α-methylstyrene (MS) are homogeneous up to considerably higher molecular weights than are mixtures of the corresponding homopolymers. This result agreed with predictions made earlier by Krause[5] and by Meier[6] using two different theoretical approaches to microphase separation in block copolymers. In the present work, we tested this prediction for triblock copolymers of types S-MS-S and MS-S-MS and we also attempted to test the prediction[5] that triblock copolymers are homogeneous to higher molecular weights than are diblock copolymers of the same composition. In addition, a detailed comparison was made between the experimental results and the theoretical predictions[5] in order to highlight possible defects in the theoretical treatment.

Experimental Section

Polymer Synthesis. The block copolymers were prepared by anionic polymerization in tetrahydrofuran at −78 °C, using 2-butyllithium as initiator for the diblock and the S-MS-S triblock copolymers and sodium naphthalene for the MS-S-MS triblock copolymers. When a monomer was added to the reaction vessel, it was always added slowly, by distillation. Because of the high molecular weights of most of our polymers, extreme precautions were required to exclude impurities from all apparatus, solvent, and reagents used in the polymerizations.[7-9]

Characterization of Molecular Weight Distribution and Composition. Approximate molecular weight averages of the block copolymers were obtained using first a Waters Associates Model 200 Gel Permeation Chromatograph, GPC, and later a Water Associates Anaprep GPC. The GPC columns, usually five in number, ranging from 2×10^3 to 7×10^5 Å in exclusion limit, were calibrated with polystyrene standards and molecular weights of the copolymers were calculated as if the copolymers were pure polystyrene. Hansen and Shen,[10] who worked with S-MS-S and MS-S-MS triblock copolymers, have discussed the validity of this procedure and concluded that the resulting molecular weights should be very realistic. The compositions of the block copolymers were calculated from the polymerization conditions and were then checked using infrared spectroscopy (IR) and high resolution proton magnetic resonance (NMR). IR data were obtained using a Perkin-Elmer Model 621 spectrophotometer using 10% solutions of polymer in benzene. The ratio of the absorption at 1236 cm^{-1} to that at 906 cm^{-1} was used for the determination of % MS in each sample;[10] a calibration curve was obtained using mixtures of the homopolymers. NMR data were obtained using a Varian T-60A NMR spectrometer using 10% solutions of polymer in CCl_4 containing a small amount (one drop in 1 mL) of dioxane as internal reference. The ratio of the area under the peak in the region 2.7 to −0.8 ppm to that in the region 7.75 to 5.75 ppm was used for the determination of % MS in each sample;[10] a calibration curve was obtained using mixtures of the homopolymers.

Sample Fractionation. Some block copolymer samples whose GPC's indicated very asymmetric or two-peaked molecular weight distributions were crudely fractionated, partly to obtain more monodisperse samples and partly to obtain some information about composition distribution. Fractionations were performed using precipitation methods; a 0.3 to 0.5% solution of polymer in benzene or toluene was prepared and methanol was used as precipitant. A maximum of three fractions was obtained from each sample. The results of two such fractionations are shown in Table I and in Figures 1a and 1b.

Determination of Glass Transition Temperatures. DTA and DSC thermograms were obtained on the block copolymer samples using four different instruments during the course of this work. On any instrument, the first run on a sample was usually discarded because it depended on sample history and was not reproducible; the results of the first two reproducible runs were usually recorded. In Table II, Method A refers to a homemade DTA instrument built around a DuPont 900 DTA cell and presented to us by the Exxon Corporation; Method B refers to a Fisher Thermolyzer Model 300 QDTA; Method C refers to a DuPont 900-DSC module; and Method D refers to a Perkin-Elmer DSC-2. Heating rates varied from 15 to 25 °C/min, depending on the instrument. Method E in Table II refers to volume dilatometry using glass dilatometers with mercury as the indicating fluid and with 1.291 mm i.d. precision bore capillary tubing which was calibrated before it was attached to the dilatometer bulb into which pieces of polymer film were then placed for a dilatometric run.

Results and Discussion

Sample Fractionation. Figures 1a and 1b, in conjunction with Table I, indicate that block copolymers with an obvious two-peaked GPC distribution have the expected large composition distribution (Figure 1a). It was unexpected to find a substantial fraction of essentially pure poly(α-methylstyrene), 1F3, in sample 1. This can be explained by assuming that there was a substantial number of monoanions as well as dianions formed by the reaction of sodium naphthalene with styrene at the beginning of the polymerization of this sample, that these monoanions attained half of the molecular weight of the dianions before the MS monomer was added to the reaction mixture, and that both types of anions added MS monomer. Sample 2, which started with a broad but not two-peaked GPC distribution, also contained essentially pure polystyrene, 2F3. These results indicate that double-peaked and broad distributions observed in the GPC of anionically polymerized block copolymers are very likely to indicate the presence of homopolymer, perhaps even both homopolymers. It should be noted that these fractionations, crude as they were, apparently proceeded by molecular weight, not by composition. This can be observed from Table I, in which $\overline{M}_w$ drops smoothly with fraction number in each fractionation, but composition does not show a consistent trend. All of the fractions, therefore, may have a considerable composition distribution which is not visible in the GPC diagrams of Figures 1a and 1b. This cautionary remark is necessary not only

Table I
Fractionation Data for Two MS-S-MS Copolymers

Sample	Wt. of fraction, g	% MS			$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
		Stoichiometric	IR	NMR		
1	*a*	37			6.7	1.31
1F1	1.75	37	26	24	9.7	1.27
1F2	1.5	37	4		5.0	1.22
1F3	0.75	37		95	4.4	1.26
2	*b*	49			5.6	1.48
2F1	2.83	49	57	53	5.5	1.41
2F2	2.1	49	50	41	4.0	1.35
2F3	0.55	49	7		2.1	1.07

[a] 4.4 g were used for fractionation. [b] 5.9 g were used for fractionation.

Table II
Sample Characterization and Calculations

Sample	Type	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$	% MS (w/w)		T_g		$(\chi_{AB})_{cr}$	
					IR	NMR	Value, °C	Method	$\overline{M}_w$	$\overline{M}_z$
DB1	S-MS	2.6	1.10	1.10	59	51	118 to 125 (broad)	A	0.0058	0.0054
							98, 101	B		
							108, 121, 137	C		
							125 (not sharp)	D		
							Very broad	E		
DB2	S-MS	6.4	1.20	1.17	60	56	101 and 170	A	0.0024	0.0021
							112 and 180	D		
							102 and 162	E		
DB3[a]	S-MS	9.4	1.12	1.14	36		105	A	0.0017	0.0015
DB4	S-MS	10.6	1.14	1.12	60	57	103 and 170	A	0.0014	0.0013
							106	B		
							112 and 180	D		
							102 and 164	E		
DB5	S-MS	13.0	1.6	1.5	58	44	110, 108	B	0.0012	0.0007
							110 and 180	D		
TB1	S-MS-S	12.7	1.3	1.3	51	52	104, 105	B	0.0017	0.0013
							112 and 180	D		
TB2	S-MS-S	16.6	1.16	1.18	50	51	109, 111	B	0.0013	0.0011
							113 and 180	D		
							108 and 163	E		
TB3	S-MS-S	17.0	1.9	1.4	52		109	B	0.0013	0.0009
							112 and 180	D		
TB4[b]	MS-S-MS	4.0	1.4	1.3	50	41	Very broad	D	0.0056	0.0043
TB5[c]	MS-S-MS	5.5	1.4	1.3	58	53	Very broad	D	0.0041	0.0032
TB6[a]	MS-S-MS	6.0	1.4	1.2	25	18	111	D	0.0052	0.0042
TB7	MS-S-MS	6.3	1.6	1.4	34	24	108	D	0.0042	0.0031
TB8[d]	MS-S-MS	9.7	1.3	1.2	26	24	111	D	0.0030	0.0024
TB9	MS-S-MS	11.6	1.2	1.2	40	32	112 and 188	D	0.0021	0.0016

[a] A fraction from a sample not discussed in Table I. [b] Fraction 2F2 in Table I. [c] Fraction 2F1 in Table I. [d] Fraction 1F1 in Table I.

because the presence of homopolymer is expected to change the thermodynamic tendency toward microphase separation in block copolymers[11] but also because this tendency has already been observed[12,13] in the styrene–α-methylstyrene system.

Sample Characterization and Calculations. Table II gives data on the diblock and triblock copolymer samples to be discussed in this paper. None of these had an obviously double-peaked distribution. Samples DB2, DB3, and DB4 in Table II are respectively identical with samples D1, D3, and D2 of ref 4. Molecular weight and composition values are slightly different because of improved instrument calibrations. Five of the samples in Table II are actually fractions of more polydisperse samples; three of these were shown in Table I and are so identified. For some samples, the composition determined using IR was up to 10% (as % MS in the sample) different from that determined by NMR. In those cases, the average of the two values was used in further considerations and calculations.

When several T_g's are shown in Table II for the same sample by the same method, these may refer to a range of values calculated from a single experiment (118 to 125 °C), different values obtained in different experiments (98, 101 °C), or two different T_g's observed in a single experiment (101 and 170 °C). For a number of samples, using particular measuring instruments, only a single T_g, in the usual range of the polystyrene T_g, was observed. In some cases, such as samples DB4 and TB2, the poly(α-methylstyrene) transition was observable using a different instrument. The T_g of the poly(α-methylstyrene) phase seems to be intrinsically harder to observe using DTA or DSC than that of the polystyrene phase; therefore, it is not surprising that only the polystyrene T_g was observed in most samples that contained less than 50% α-methylstyrene, i.e., samples DB3, TB6, TB7, and TB8.

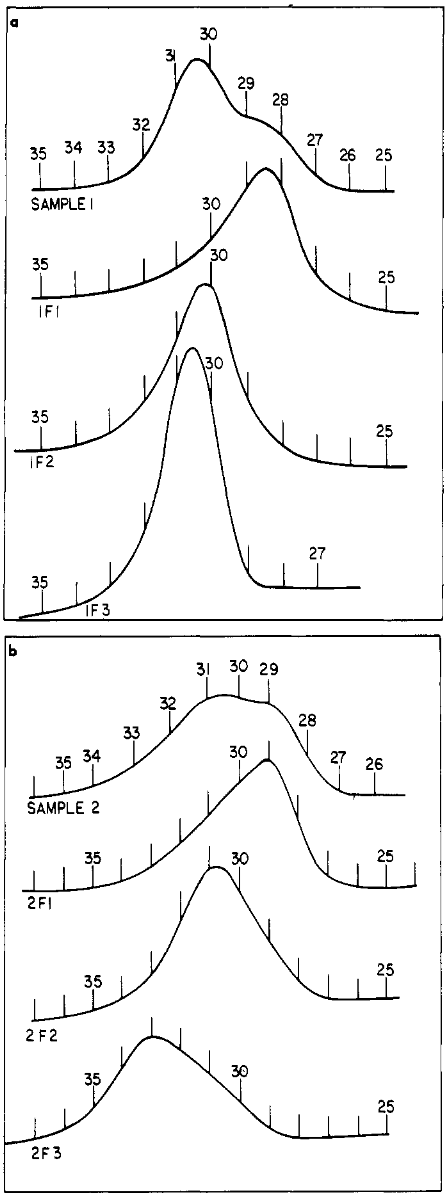

Figure 1. (a) GPC of sample 1 and its fractions. (b) GPC of sample 2 and its fractions.

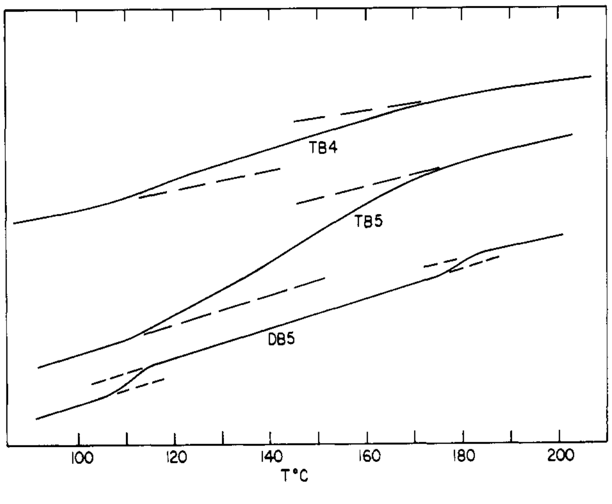

Figure 2. DSC curves of samples TB4, TB5, and DB5.

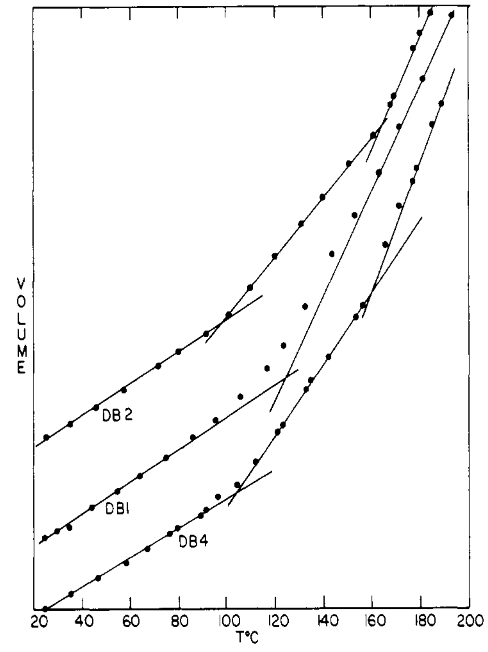

Figure 3. Dilatometric curves of samples DB1, DB2, and DB4.

We would say that the T_g data indicate microphase separation in samples DB2, DB3, DB4, DB5, TB1, TB2, TB3, TB6, TB7, TB8, and TB9. Sample DB1, although it exhibited the T_g of polystyrene in several runs by Method B and in one run by Method C, was considered homogeneous because it usually exhibited very broad transitions, intermediate between those of the homopolymers. Samples TB4 and TB5 were also considered homogeneous; their DSC curves, contrasted with that of sample DB5 in Figure 2, indicate a very broad transition, ranging all the way from that of polystyrene to that of poly(α-methylstyrene). Instrument D, a Perkin-Elmer DSC-2, and Method E, volume dilatometry, seemed to be the best of the methods used in this work of observing all T_g's present in the samples. Figure 3 shows some dilatometric data for samples DB1, DB2, and DB4.

Since it is known that poly(α-methylstyrene), PMS, degrades at temperatures not far above 200 °C[14] and that the presence of PMS enhances the thermal degradation of polystyrene, PS,[15] several samples of block copolymer were examined after the thermal cycling needed for T_g determination. In general, the GPC data obtained before and after cycling showed no evidence of degradation for any of the samples examined. Figure 4 shows one of the sets of data obtained.

The last two columns in Table II are labeled $(\chi_{AB})_{cr}$, the interaction parameter that would be necessary between PS and PMS if that block copolymer sample were at the exact point of equilibrium between homogeneous sample and sample in which microphase separation had taken place. Values of $(\chi_{AB})_{cr}$ were calculated using the equation of Krause:[5]

$$(\chi_{AB})_{cr} = \frac{zV_r}{(z-2)V_A n_A^c v_B^c}\left\{-\ln (v_A^c)^{v_A^c}(v_B^c)^{v_B^c} + 2(m-1)\frac{(\Delta S)_{dis}}{R} - \ln (m-1)\right\} \qquad (1)$$

where z = lattice coordination number (assumed = 8); V_r = volume of a lattice cell, the reference volume; V_A = volume of a repeat unit of A (assumed = V_r); n_A^c = number of repeat units of A per molecule; v_A^c, v_B^c = volume fractions of A and B in each molecule (ASSUMED = weight fraction); m = number of blocks of A + number of blocks of B per molecule; and $(\Delta S)_{dis}/R$ = disorientation entropy gain on fusion per repeat unit in the polymer

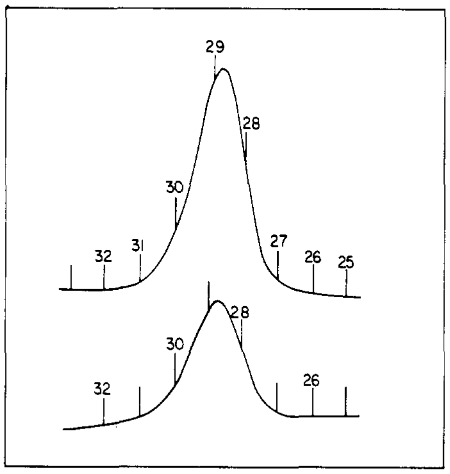

Figure 4. GPC of sample DB3 before and after several runs using Method E.

The value used for $(\Delta S)_{\rm dis}/R$ in the calculations was 1.0, not only for the reasons discussed previously[5] but also because this is the value calculated from the experimentally determined entropy of fusion of isotactic polystyrene after subtracting the entropy connected with the volume change on fusion.[16] Since the value of $n_{\rm A}{}^{\rm c}$ used in the calculations depends on the molecular weight of the block copolymer sample as well as on its composition, one may wonder which molecular weight average to use for those samples which are far from monodisperse. We have made the calculation using both $\bar{M}_{\rm w}$ and $\bar{M}_{\rm z}$ because it is hard to tell which of these molecular weight averages has the greater effect on phase separation, even in the case of homopolymers. Tompa[17] has discussed the theoretical reasons for choosing $\bar{M}_{\rm w}$, while, more recently, Koningsveld[18] has discussed reasons for choosing $\bar{M}_{\rm z}$. For those samples in Table II whose $\bar{M}_{\rm z}/\bar{M}_{\rm w} \approx 1.1$, the choice of molecular weight average used in the calculations made little difference. This is only one of the reasons why it is preferable to work with reasonably monodisperse polymers when attempting to compare experimental observations with theoretical predictions of phase separation.

Implications of the Data in Table II. It was stated above that all samples *except* DB1, TB4, and TB5 could be assumed to have undergone microphase separation, judging from the values of $T_{\rm g}$ obtainable by the various methods. Since the calculated value of $(\chi_{\rm AB})_{\rm cr}$ for each sample implies that this sample will undergo microphase separation if the actual $\chi_{\rm AB}$ between the homopolymers is greater than $(\chi_{\rm AB})_{\rm cr}$, let us assume that the actual value of $\chi_{\rm AB}$ is below the lowest $(\chi_{\rm AB})_{\rm cr}$ of all mixed samples and above the highest $(\chi_{\rm AB})_{\rm cr}$ of all samples that have undergone microphase separation. Using these criteria, we reach the following conclusions. Considering diblock copolymers only, $\chi_{\rm AB}$ for PS and PMS is between 0.0024 and 0.0058 using $\bar{M}_{\rm w}$ and between 0.0021 and 0.0054 using $\bar{M}_{\rm z}$. Considering triblock copolymers, either alone or in conjunction with diblock copolymers, the results are more complex. Using $\bar{M}_{\rm w}$, it seems as if $\chi_{\rm AB}$ must be less than 0.0041 but greater than 0.0052, while values obtained using $\bar{M}_{\rm z}$ indicate that $\chi_{\rm AB}$ must be less than 0.0032 but greater than 0.0042. These contradictory conclusions have one of two possible causes: (1) samples with $\bar{M}_{\rm w}/\bar{M}_{\rm n} > 1.3$ may be so polydisperse that they should not be used for detailed comparison with theoretical predictions made for monodisperse polymers, or (2) samples whose $(\chi_{\rm AB})_{\rm cr}$ is close to $\chi_{\rm AB}$ may appear in a metastable phase state at times, i.e., phase separated when the stable state is homogeneous, or vice versa.

It was stated above that there is evidence that the presence of homopolymer in a block copolymer promotes phase separation, and we presented evidence in Table I that at least some of our less monodisperse block copolymers contained homopolymer. Therefore, it is quite likely that our more polydisperse samples exhibited microphase separation at values of molecular weight and composition at which a monodisperse sample would have been homogeneous. If we then throw out all data from samples in Table II with $\bar{M}_{\rm w}/\bar{M}_{\rm n} > 1.3$ which exhibited microphase separation, that is, samples DB5, TB3, TB6, and TB7, then we find $\chi_{\rm AB}$ between 0.0041 and 0.0030 using $\bar{M}_{\rm w}$ and between 0.0032 and 0.0024 using $\bar{M}_{\rm z}$.

The presence of metastable phase states under some circumstances was shown by sample DB1, whose intermediate $T_{\rm g}$ by methods A, D, E, and usually C indicated that the blocks were mixed, but where the $T_{\rm g}$ of polystyrene was observed by Method B and once by Method C. Different samples may exhibit metastable phases with greater or lesser ease.

At any rate, the data indicate that, if eq 1 is assumed correct and used as specified, $\chi_{\rm AB}$ for PS and PMS is most likely between 0.0030 and 0.0041 (using $\bar{M}_{\rm w}$) or between 0.0024 and 0.0032 (using $\bar{M}_{\rm z}$). Data obtained by Robeson et al.[12] on S-MS diblock copolymers can be used to narrow this range, at least for the $\bar{M}_{\rm w}$ data. Their three samples, ranging in $\bar{M}_{\rm w}$ from 8.0×10^4 to 4.20×10^5, with $\bar{M}_{\rm w}/\bar{M}_{\rm n} \leq 1.08$, 50 mol % MS, each had a dynamic mechanical $T_{\rm g}$ intermediate between that of PS and PMS. In other words, none of their samples was phase separated. Using only the highest molecular weight sample, one obtains $(\chi_{\rm AB})_{\rm cr} = 0.0036$, i.e., their data indicate that $\chi_{\rm AB}$ must be less than 0.0036. Combining this with our $\bar{M}_{\rm w}$ data for $(\chi_{\rm AB})_{\rm cr}$, we find, leaving out data on phase-separated samples with $\bar{M}_{\rm w}/\bar{M}_{\rm n} > 1.3$, that $\chi_{\rm AB}$ for PS and PMS must be between 0.0036 and 0.0030. This compares well with the value of 0.002 originally predicted by Krause[5] on the basis of calculated solubility parameters for PS and PMS. This further implies that the theoretical treatment of microphase separation in block copolymers leading to eq 1 is reasonably satisfactory.

One may attempt to use the block copolymer data to test this theoretical treatment in greater detail by separating the data on diblock copolymers from those on triblock copolymers and performing some additional calculations. Equation 1, because it contains the total number of blocks in the block copolymer, m, predicts different values of $(\chi_{\rm AB})_{\rm cr}$ for diblock and triblock copolymers which have the same molecular weight and composition. If we pretend, for the moment, that all the triblock copolymers were really diblock copolymers, we obtain different values of $(\chi_{\rm AB})_{\rm cr}$ than those shown in Table II. If this is done, and if the data on samples with $M_{\rm w}/M_{\rm n} > 1.3$ are again removed from consideration, then $\chi_{\rm AB}$ for PS and PMS must be between those calculated for samples TB5 and TB8, that is, between 0.0027 and 0.0020 if these samples are considered as diblock copolymers in eq 1 using $\bar{M}_{\rm w}$; this contrasts with the value of $\chi_{\rm AB}$ between 0.0041 and 0.0030 calculated assuming, properly, that these samples are triblock copolymers. To compare these calculations with those for the actual diblock copolymers, let us recall that $\chi_{\rm AB}$ for PS and PMS must lie between $(\chi_{\rm AB})_{\rm cr}$ of sample DB2, the lowest molecular weight phase separated diblock copolymer, and $(\chi_{\rm AB})_{\rm cr}$ of Robeson et al.'s[12] highest molecular weight homogeneous diblock copolymer, that is, between 0.0036 and 0.0024. This leaves $\chi_{\rm AB}$ for PS and PMS between 0.0024 and 0.0027 if all block copolymers are assumed to be diblock copolymers in eq 1, and between 0.0030 and 0.0036 if eq 1 is used as derived, considering the actual number of blocks in the block copolymers. The differences are not great, and it may not be possible to test the accuracy of the particular assumptions leading to the terms associated with the number of blocks in the block copolymer molecules in eq 1 by testing for microphase separation in diblock and triblock copolymers.

A further and more exacting test of the assumptions underlying eq 1 is given by comparing χ_{AB} of PS and PMS obtained from the block copolymer data above with that obtained previously[4] from data on phase separation in mixtures of the PS and PMS homopolymers. The value obtained from those data was 0.0013 exactly. In this work, using eq 1 on the data for all narrow distribution block copolymers, we obtained a value between 0.0030 and 0.0036, two-and-a-half to three times that obtained for homopolymer mixtures. This is fairly good agreement, but it is not exact, so it is of interest to find out whether any simple changes can be made in the assumptions leading to eq 1. The easiest assumption to deal with is the one leading to the term that contains $(\Delta S)_{\mathrm{dis}}/R$; this term assumes that all the disorientation entropy possible is lost on microphase separation of a sample when all the A and B units that link the blocks in each copolymer molecule are immobilized totally at a microphase surface. It was stated previously[5] that the block-linking segments may actually not be entirely immobilized, while the neighboring segments may have lost some of their disorientation entropy; it was assumed that the loss of disorientation entropy per A-B connection in the block equalled that which would be lost if two segments were totally immobilized. If this assumption is changed so that, on the average, the disorientation entropy of only one segment is lost per A-B connection on microphase separation, then the factor of 2 disappears from the term containing $(\Delta S)_{\mathrm{dis}}/R$ in eq 1 and new calculations of the $(\chi_{AB})_{\mathrm{cr}}$ of each block copolymer in Table II can be made. Using the results of the new calculations, χ_{AB} of PS and PMS comes out between 0.0022 and 0.0015, in good agreement with the homopolymer results.

It is interesting to note, in this connection, some recent work by Toporowski and Roovers[19] on low molecular weight diblock and triblock copolymers of styrene and isoprene. These authors, in their comparison of phase separation data with the theory of Krause,[5] also concluded that the χ_{AB} found for polystyrene and polyisoprene by using eq 1 in approximately the same way in which it was used in the present work agreed reasonably well with that obtained from homopolymer data. They indicated, however, that it was very difficult to determine the boundary between block copolymers that form a single phase and those that form two phases from their DSC data. They found some very broad transitions, similar to that of our samples TB4 and TB5, especially in their lowest molecular weight samples, $\overline{M}_n \approx 5450$. For this reason, their data probably also cannot be used to ascertain whether this theoretical treatment distinguishes properly between diblock and triblock copolymers.

Conclusions

1. The available data on microphase separation in diblock and triblock copolymers of styrene and α-methylstyrene, in conjunction with eq 1, taken from a theoretical treatment of microphase separation in block copolymers by Krause,[5] indicate that the interaction parameter between polystyrene and poly(α-methylstyrene) lies between 0.0030 and 0.0036.

2. The available data were not sufficient to allow a decision about the adequacy of the differentiation between diblock and triblock copolymers in that theoretical treatment.[5]

3. The interaction parameter calculated from these data can be made to agree with the results of an analysis of homopolymer–homopolymer phase separation data by assuming that only a single polymer segment is, on the average, completely immobilized at every A-B block junction when microphase separation occurs.

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